

## **2.4 Membranes: Nanofiltration and Affinity**

### **2.4.1 Background**

The term “membrane” covers a wide range of processes, including those used for gas/gas, gas/liquid, liquid/liquid, gas/solid, and liquid/solid separations. Membrane technology is well-established and is used in many processes. Membrane production is a large-scale operation. Membranes are used for the separation of radionuclides as well as other contaminants. This section discusses three nanotechnologies that are often used in the filtering processes and show great potential for applications in remediation.

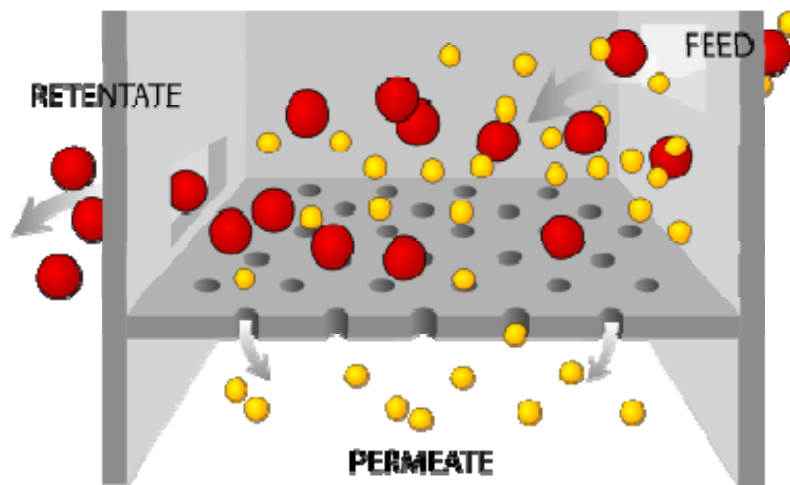
1. *Nanofiltration* (and its sibling technologies: reverse osmosis, ultrafiltration, and microfiltration), is a fully-developed, commercially-available membrane technology with a large number of vendors. Nanofiltration relies on the ability of membranes to discriminate between the physical size of particles or species in a mixture or solution and is primarily used for water pre-treatment, treatment, and purification (Van der Bruggen and Vandecasteele 2003, Rautenbach and Groeschl 1990, Rautenbach et al. 1997, Atkinson 2002, Costa and de Pinho 2006). There are approximately 600 companies worldwide offering membrane systems.
2. *Electrospinning* is a process utilized by the nanofiltration process, in which fibers are stretched and elongated down to a diameter of about 10 nm. The modified nanofibers that are produced are particularly useful in the filtration process as an ultra-concentrated filter with a very large surface area. Studies have found that electrospun nanofibers can capture metallic ions and are continually effective through re-filtration.
3. *Surface modified membrane* is a term used for membranes with altered makeup and configuration, though the basic properties of their underlying materials remain intact.

With the global water market valued at over \$300 billion, and water supplies becoming an important international issue, nanofiltration is anticipated to have a very important role in the future. In contrast to the types of filtration that rely on size discrimination, affinity membranes use chemical recognition between the components of the membrane and components of solution to effect separation. Affinity membranes and related technologies are well-established and find their primary markets in the biomedical and biotechnology industries.

### **2.4.2 Nanofiltration Membranes**

Nanofiltration is one of a group of similar membrane processes (including reverse osmosis, ultrafiltration, and microfiltration) used to separate components of a liquid mixture. These four processes are best understood together and as a continuum in terms of the size of particles that can be removed from a mixture.

In the regular particle filtration of a liquid containing entrained particles, the liquid mixture is forced (by gravity or applied pressure) through a filter medium that has pores or passages of a size that allows the liquid and small particles to pass through, but prevents passage of larger particles. A paper coffee filter is an example of a regular particle filtration. The paper filter allows passage of the water containing dissolved or extremely small material, but prevents passage of the larger coffee grounds. Smaller pores or passages in the filter medium prevent larger particles from passing through with the liquid. Figure 5 provides a graphical representation of the generalized filtration process.



**Figure 5. General representation of the filtration process**

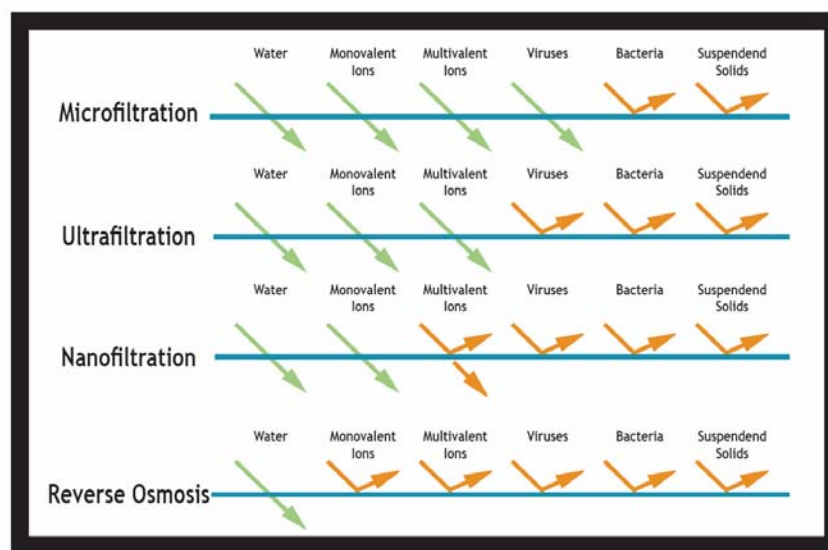
There are two basic types of filters: depth filters and membrane filters. Depth filters have a significant physical depth and the particles to be retained are captured throughout the depth of the filter. Depth filters often have a labyrinthine three-dimensional structure, with multiple channels and heavy branching so that there is a large pathway through which the liquid must flow and by which the filter can retain particles. Depth filters have the advantages of low cost, high throughput, large particle retention capacity, and the ability to retain a variety of particle sizes. However, they can suffer from entrainment of the filter medium, uncertainty regarding effective pore size, some uncertainty regarding the overall integrity of the filter, and the risk of particles being mobilized when the pressure differential across the filter is large.

The second type of filter is the membrane filter, in which depth is not considered important. The membrane filter uses a relatively thin material with a well-defined maximum pore size and the particle retaining effect takes place almost entirely at the surface. Membranes offer the advantage of having well-defined effective pore sizes, can be integrity tested more easily than depth filters, and can achieve more filtration of much smaller particles. They tend to be more expensive than depth filters and usually cannot achieve the throughput of a depth filter. Filtration technology has developed a well-defined terminology that has been well addressed by commercial suppliers; the American Standard Test Method (ASTM) has developed a standard (ASTM D6161-05) (ASTM

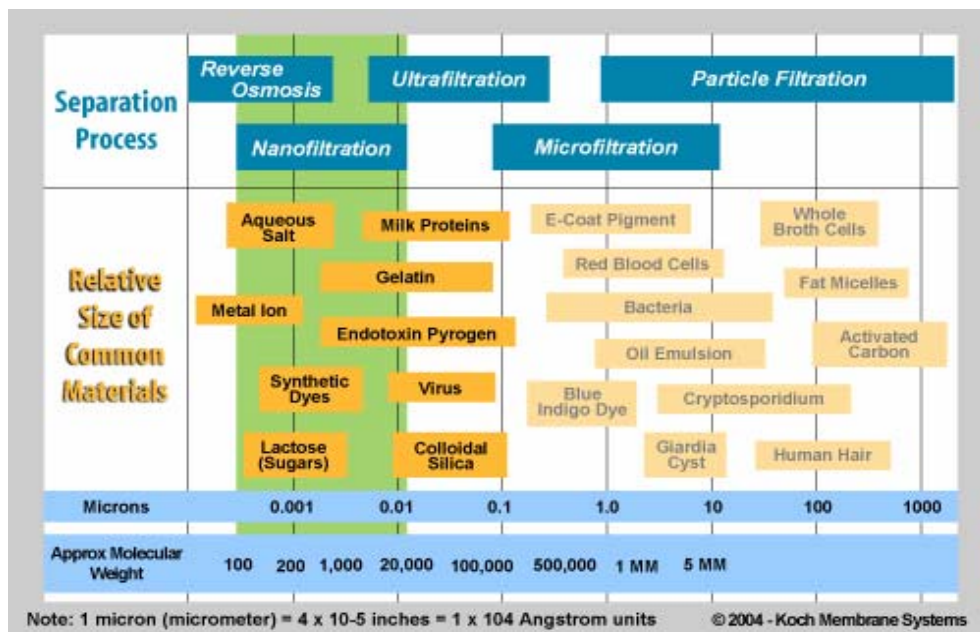
2007) that addresses the terminology used for microfiltration, ultrafiltration, nanofiltration, and reverse osmosis membrane processes.

Reverse osmosis, nanofiltration, ultrafiltration, and microfiltration are all membrane processes able to remove small particles or soluble species. They all work on exactly the same principle as regular particle filtration, but the distinguishing feature between them is their effective pore size, and thus, the minimum size of particle that will be rejected by the membrane; reverse osmosis membranes reject all but the very smallest species (small soluble organic species that are not otherwise considered even to be “particles”), while microfiltration allows considerably larger particles to pass through. Figure 6 provides a graphic representation of the process characteristics of the four membrane processes, and Figure 7 provides a graphic representation showing the size range and approximate molecular weight range where each of the four membrane filtration technologies finds its application.

Regular particle filtration will reject particles down to about the one micron (1,000 nm) size range. If filtration to reject particles smaller than this limit is required, microfiltration should first be considered. Microfiltration operates at the low end of familiar particle filtration, being at the limit able to retain particles above the 100 nm size range. Its separating abilities thus cease at the 100 nm limit usually associated with nanotechnology. Microfiltration can remove most suspended solids and living material, such as bacteria, but will not retain any type of dissolved solute or smaller biological material, such as viruses. Ultrafiltration is effective only to the 10 nm size range, allowing it to reject most proteins, viruses, and groundwater colloids. Nanofiltration is usually used to remove material in the 0.5-10 nm range and will reject most of the larger organic molecules, sugars, and multivalent ions, with only monovalent ions and water being able to pass through. To remove the monovalent ions, reverse osmosis membranes are required; these will reject almost all material, except water and simple organic species (such as very short chain alcohols and acids).



**Figure 6. Membrane process characteristics**



**Figure 7. Size range for filtration separation processes**

Benefits of water treatment nanofiltration include:

- Lower operating costs,
- Lower energy costs,
- Lower discharge and less wastewater than reverse osmosis,
- Reduction of total dissolved solids (TDS) content of slightly brackish water,
- Reduction of pesticides and VOCs (organic chemicals),
- Reduction of heavy metals,
- Reductions of nitrates and sulfates,
- Reduction color, tannins, and turbidity,
- Hard water softening,
- Being chemical-free (i.e., does not use salts or chemicals), and
- Water pH after nanofiltration is typically non aggressive.

For radionuclide treatment applications, nanofiltration and ultrafiltration have been investigated as an ultra low-level analytical tool to separate actinides from other ionic species in high-level radioactive waste solutions, and as a possible treatment option for waste streams from the Los Alamos National Laboratory Plutonium Treatment Facility (Smith 1993). In these applications, the nanofiltration and ultrafiltration membranes are coupled with water-soluble chelating polymers (WSCP). WSCPs are polymers engineered to contain both highly selective chelating functionalities to bind with targeted metal ions, and solubilizing functionalities to allow the polymer to dissolve in water (Smith et al. 1995). The polymer's overall size is large enough that it exceeds the rejection limit for an ultrafiltration membrane. When the unchelated polymer is introduced into a solution that contains the target ions for which the chelating groups

were designed, the polymer binds with these target ions and nothing else. The chelated polymer can then be separated from the solution (and all other ions in the solution) by ultrafiltration; the chelated target ions can be separated from the polymer by adjusting the solution chemistry; and the regenerated water-soluble chelating polymer can be recycled (Jarvinen 1995). In these applications, ultrafiltration combined with WSCP has the advantage of being aqueous-based (such as ion exchange resins), has a high throughput and rapid kinetics (like two-phase liquid-liquid extraction systems), but does not have the disadvantage of using organic solvent-based extractants.

WSCPs with molecular weights in the 100,000 range have been prepared based on polyacrylic acid or polyethyleneimine with functional groups of phosphonic acid, acylpyrazolone acid, and hydroxamic acid. In acidic nitrate and acidic chloride solutions, these functional groups have a high affinity for actinides and a low affinity for alkali metals and alkaline earths. The concentration of polymer is typically 1-2%, with the ultrafiltration membrane typically having 10-100  $\mu\text{m}$  pores (Gibson 1994, Smith 1993). This technology has been tested at bench scale for the removal of heavy metal ions from electroplating waste streams. Development continues (Moreno-Villoslada and Rivas 2002, Rivas et al. 2003, Rivas et al. 2006, Tomida et al. 1994, Kawano et al. 2002), though dendrimers may compete as a chelating moiety in the future if their costs decrease.

### ***Summary of Environmental Potential***

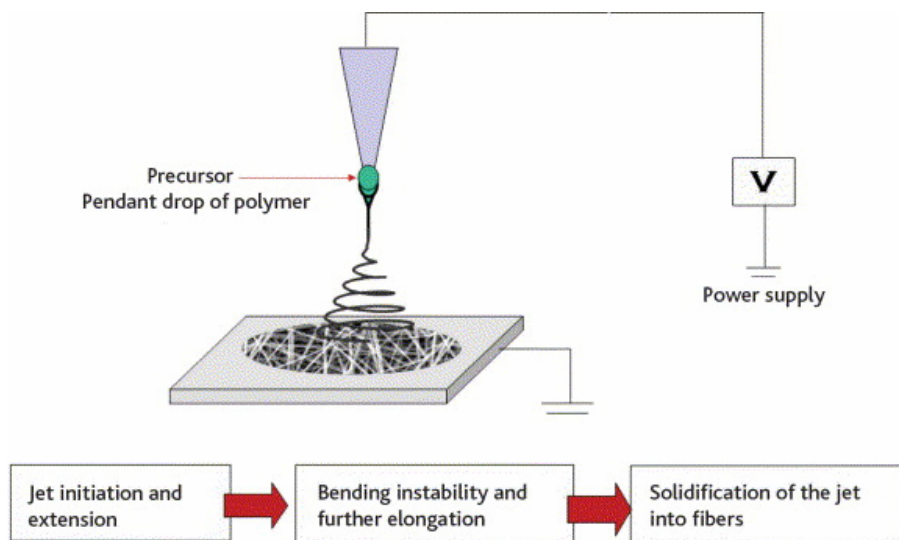
Nanofiltration is an established technology with numerous equipment developers, manufacturers, and vendors. The major application is in reverse osmosis for desalination and production of high purity water for specialized industrial uses, with small applications for wastewater treatment. While current and past development has relied predominantly on size exclusion effects, the promise of nanotechnology is that specific chemical and physical behavior can be engineered into the materials, and that the slow flow rates typical of reverse osmosis and nanofiltration can be overcome—allowing the energy requirements and production costs for the production of pure water to be greatly reduced. The general industrial uses of filtration technology should support developments that will allow spin-off applications for environmental uses; a significant effort is being made to apply nanotechnology developments of filtration technology to the production of potable water in economically challenged arid regions. The primary environmental applications are likely to be “end-of-pipe” and polishing uses. Nanofiltration combined with water-soluble chelating polymers has been investigated for the removal of radioactive species from aqueous waste streams (Smith 1993, Smith et al. 1995).

#### ***2.4.4 Electrospun Fibers***

Electrospinning is a process for making nanofibers with diameters down to about 10 nm. The technology produces the nanofibers from polymer solutions or melts, with the extreme elongation and narrowing of the fiber occurring as a result of electrostatic repulsion. Electrospinning has the characteristics of both the commercial electrostatic spraying technique and the commercial spinning of fibers, each of which is a long established technology in its own right. Electrostatic spraying is a coating technology,

over a century old, involving atomizing a liquid from a spray gun and imparting an electrical charge to the droplets by using an electrode placed at the end of a spray gun. The electrode typically operates in the 30 to 140 kilovolt range with a current of 0 to 225 microamperes. The droplets are attracted toward a target that is either grounded or has a positive charge, and produces a uniform coating of liquid (frequently paint). The electrostatic spraying approach can also be used as a surface modification technique to introduce nanoparticles onto fibers or other surfaces by spraying solutions that contain only about one particle per droplet.

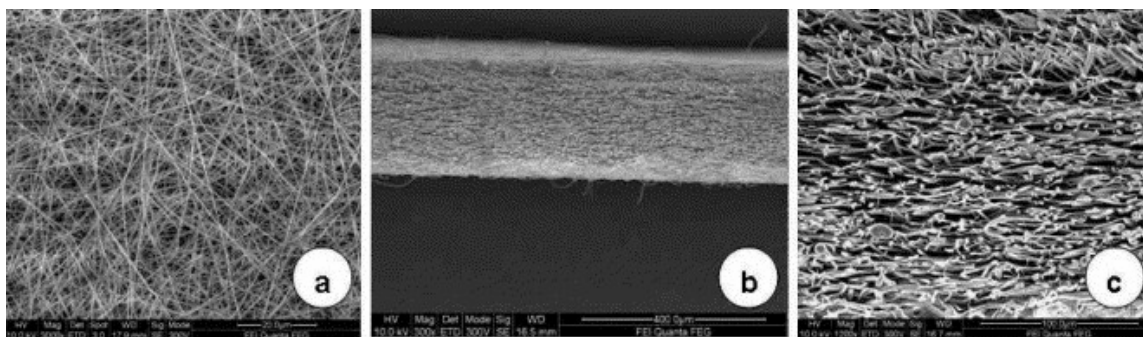
In comparison, electrospinning (first patented by Antonin Formhals in 1934) uses the electrical charge to form a mass of fine polymer filaments. In electrospinning, a polymer solution or melt is driven through a spray gun nozzle and forms a droplet at the tip. When the voltage is applied to the nozzle, the droplet is stretched; if the viscosity of the material is sufficiently high, the breakup encountered in electrostatic spraying does not occur. Instead, a thin, charged liquid jet is formed. The jet elongates and is whipped continuously by electrostatic repulsion, forcing it to follow a spiral path toward the oppositely charged or grounded collector. The whipping action helps to elongate the jet much further to a diameter on the order of tens of nanometers. Figure 8 illustrates the basic process. Fibers are formed either by the melt cooling or the solvent evaporating from the polymer solution. Nanoparticles can be mixed into, or produced directly in, the polymer solution and spun with the fibers (Lee et al. 2005). Nanofibers produced in this way have many potential applications, including high efficiency filter media, as nanocomposite materials for water treatment membranes, catalysis, hydrogen storage, or in biomedical applications (such as drug release carriers or artificial tissue).



**Figure 8. Basic principle of electrospinning**

Investigations into the potential of electrospun fibers for water treatment have mainly focused on their use in membranes, where the massive surface area (illustrated in Figure 9) offers special advantages. Ki et al. (Ki et al. 2007) examined membranes of a nanofibrous blend of silk fibroin and wool keratose and found that it had an exceptional performance for the adsorption of metal ions, that its adsorption capacity was maintained after several desorption and re-adsorption cycles, and that it is very suitable for removing and recovering heavy metal ions from water, potentially as an affinity membrane.

Ramakrishna et al. (Ramakrishna et al. 2006) reviewed electrospun nanofibers from the perspective that their porous nature and large surface-to-volume ratio gives them the potential for use in various applications where high porosity is desirable. They noted that electrospinning has an advantage of comparatively low cost with relatively high production rate, that the unique ability to produce nanofibers of different materials in various fibrous assemblies, and that the ability to form porous fibers means that the surface area of the fiber mesh can be increased tremendously. Since the fibers can be surface functionalized, affinity membranes can easily be formed with the potential for application in the removal of heavy metals from wastewater. They concluded that electrospinning may well be one of the most significant nanotechnologies of the 21<sup>st</sup> century.



**Figure 9. An electrospun polysulphone membrane: (a) surface; (b) cross-section; and (c) magnified cross-section images**

Sang et al. (Sang et al. 2008) examined various filtration modes for using an electrospun chloridized polyvinyl chloride nanofiber membrane (including static adsorption, direct filtration, soil-addition filtration, diatomite-addition filtration, and micellar enhanced filtration), and they concluded that the membrane, when used with micellar enhanced filtration, can be used for the treatment of the groundwater containing heavy metals (such as copper, lead, and cadmium) with high efficiency.

#### **2.4.5 Surface Modified Membranes**

Electron-beam-induced grafting is one of two methods in the category of ionizing radiation—gamma radiation from cobalt-60 is the other. Electron-beam-induced technology provides a pathway for customizing surfaces such as membranes; hence, the commercial name eMembranes (developed by the Japan Environmental Purification Research Institute). The technology allows membrane surface alternation without

changing the basic properties of the underlying bulk materials. Electron-beam machines are currently available and play a significant role in processing specialty polymeric materials. For example, electron-beam-induced grafting has existed in some form for decades; nuclear power plants have used ion exchange resins enhanced by electron-beam-induced grafting to cleanse uranium from coolants. The future materials generated with this technology is based on over 50 years of scientific research. The technology is stimulating the development of new and promising membranes. Electron-beam-induced grafting is being used by laboratories throughout the world to create surfaces, including chemical resistance, wet ability, biocompatibility, antithrombo, dyability, and antistatic properties. Grafting has also been used to produce ion exchange membranes for the removal of heavy-metal for aqueous waste streams. An emerging application is biological separations, but the basic concept also has targeted the removal of heavy metals from industrial wastewaters. There is little doubt that many new and improved products will be created to aid in the cleanup of radionuclides.

eMembrane technology is being extended to create specialized membranes for many potential applications. The ability to create specialized nano-engineered membranes opens up many envisioned possible future applications. An example of developing applications is a new water remediation technology, which could remove—in one pass—multiple contaminants such as viruses, radionuclides, heavy metals, and chlorinated solvents. A membrane could be tailored for a specific cleanup application. This would greatly reduce remediation costs and accelerate the cleanup process.

The following example of eMembrane development gives an indication of the broad and varied possibilities for developing customized membranes and material surfaces, and draws heavily from company provided literature. eMembrane's technology involves the nano-grafting of polymer chains containing selective binding functionalities. This technology can impart new and multiple polymeric material on existing materials and membranes. At the heart of the technology is the technique of electron-beam induced polymer grafting. Figure 10 provides a graphical representation of the technique showing the attachment of polymeric material.

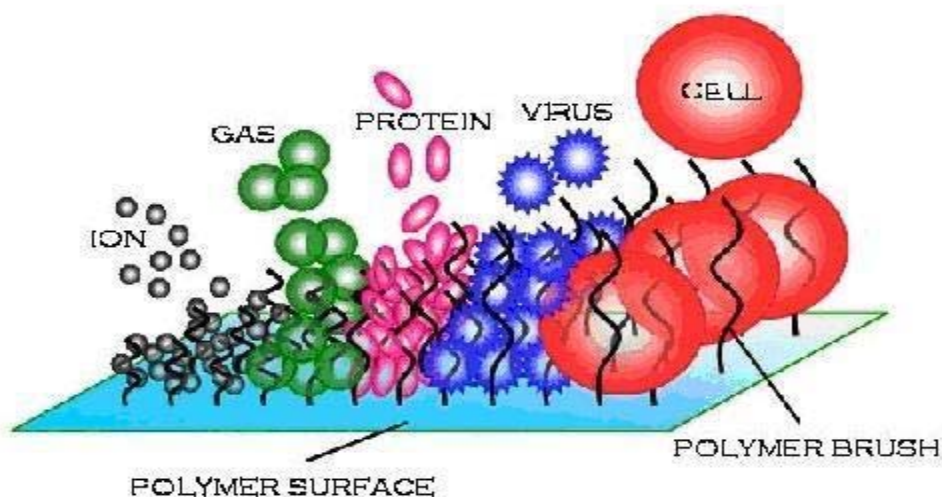


**Figure 10. Electron-beam induced polymer grafting**

The polymer chains, or filaments, typically range from 10 nm to 300  $\mu\text{m}$  long. The smallest filaments would catch ions and thus collect toxic metals from water. Larger filaments could hold gas or protein molecules, while the largest could capture whole cells or viruses in a bio-weapon defense system. There are as many as 10 trillion filaments on a square centimeter of substrate, spacing the filaments about 4 nm apart.

An electron beam irradiates a base membrane that can be made from any polymeric material. Other radiation sources, such as gamma rays, can also be used for similar radiation induced polymer grafting (Ramakrishna et al. 2005). The electron beam irradiation generates active species, or radicals, on the surface of the polymer. The active species are the sites at which other long polymer chains or brushes can be attached. The polymer brushes may contain the binding functionalities at the time of attachment, or they may be chemically functionalized after attachment has occurred. Electron beam irradiation is seen as an advantageous method of surface modification since it can occur after the basic polymer has been fabricated and does not affect the shape; by varying the electron beam energy and other process characteristics, the depth and degree of functionalization can be controlled.

eMembrane's electron-beam technology permits a density of polymer brush attachment that is extraordinary—up to 10 trillion polymer brushes per square centimeter can be attached giving a surface spacing of about 4 nm between each brush, a density far exceeding any other technique. The brushes can range from 10 to 300 nm long and can contain a variety of functionalities, allowing the production of highly tailored separation material. For example, a microporous membrane with grafted functionalized polymer brushes not only performs microfiltration (by molecular size cutoff), but the functional groups on its brushes can also simultaneously capture and remove toxic metal ions, soluble proteins, viruses, or cells from the filtrate. In effect, it has become an affinity membrane (Ofsthun et al. 1999, Zou et al. 2001, Nasef 2004, Klein 1991). Materials in a variety of shapes (e.g., film, hollow fiber, non-woven cloth, etc.) are grafted with polymer brushes that extend off the surface of the starting material. Figure 11 provides a graphical representation of the functionalized polymer surface with a variety of brushes attached to facilitate a number of separations.



**Figure 11. eMembrane-functionalized surface**

Environmentally-related applications currently under investigation by eMembrane, Inc. include:

#### Ion

- Removal, collection of heavy metal ions from fluids,
- Ultra-pure water production
- Immobilized metal affinity membrane

#### Gas

- Removal of odors or toxic gases via neutralization

#### Biological

- Tools for proteomics
- Display of multilayer of various proteins for protein-protein interaction studies
- Immobilized enzymes for proteomics, biosensors, and bioreactors
- Large-scale biologics purification

#### Cell

- Immobilized cells for proteomics studies
- Removal of bacteria
- Bioreactors, artificial organs

Radiation cross-linking of naturally occurring polymers, such as polysaccharides, is being investigated for the production of biodegradable hydrogel/nanogel. This new nanomaterial consists of individual macromolecules that are internally cross-linked by irradiation ionizing radiation.

Specifically modified nanogels are being studied for wastewater filtration. Gels containing acid groups have to bind ions, including uranium and nickel, for use in the removal of metals from aqueous media. These gels can be formulated and customized to remove most contaminants found in water.

No fate and transport studies have been conducted, nor are anticipated, since this is a process unit rather than a material. Because the technology is in the development state, no operational or maintenance parameters have been determined, and no information on impacts, hazards, efficacy, limitations, and waste management approaches is available. One of the greatest, unknown concerns is what could happen if the fibers dislodge from the surface and enter the drinking water supply.

### **2.4.6 References**

ASTM International. 2007. Standard Terminology Used for Microfiltration, Ultrafiltration, Nanofiltration and Reverse Osmosis Membrane Processes. Website. Accessed October 2007.

[http://www.astm.org/cgi-bin/SoftCart.exe/DATABASE.CART/REDLINE\\_PAGES/D6161.htm?E+mystore](http://www.astm.org/cgi-bin/SoftCart.exe/DATABASE.CART/REDLINE_PAGES/D6161.htm?E+mystore).

Atkinson, S. 2002. Nanofiltration concentrates coloured wastewater and produces potable water. *Membrane Technology*. 2002(7): 11-12.

Costa, A.R. and M.N. de Pinho. 2006. Comparison of the performance of ultrafiltration and nanofiltration in surface water treatment. *Desalination*. 199(1-3): 73-75.

Gibson, R.R., B.F. Smith, G.D. Jarvinen, T.W. Robinson, R.E. Barrans, K.V. Wilson. 1994. The Use of Water-Soluble Chelating Polymers as an Analytical Method for the Separation of Actinides in Aqueous Systems. Presentation at the Eighteenth Annual Actinide Separations Conference, Durango, CO, May 23-26, 1994.

Jarvinen, G.D., R.E. Barrans, N.C. Jr., Schroder, K.L. Wade, M.M. Jones, B.F. Smith, J.L. Mills, G. Howard, H. Freiser, S. Muralidharan. 1995. Selective Extraction of Tetravalent Actinides from Lanthanides with Dithiophosphonic Acids and Tributylphosphate. In Separations of Elements. K.L. Nash and G.R. Choppin, eds. Plenum Press, New York, 43-62.

Kawano, K., K. Hamaguchi, S. Masuda, T. Tomida. 2002. Binding Properties of a Water-Soluble Chelating Polymer with Divalent Metal Ions Measured by Ultrafiltration. Poly( $\alpha$ -acethylaminoacrylic acid). *Industrial and Engineering Chemical Research*. 41(20): 5079-5084.

Ki, C.S., E.H. Gang, I.C Um, Y.H. Park. 2007. Nanofibrous membrane of wool keratose/silk fibroin blend for heavy metal ion adsorption. *Journal of Membrane Science*. 302(1-2): 20-26.

Klein, E. 1991. Affinity Membranes: Their Chemistry and Performance in Adsorptive Separation Processes. Wiley-Interscience, Hoboken, NJ.

Lee, H.K., E.H. Jeong, C.K. Baek, J.H. Youk. 2005. One-step preparation of ultrafine poly(acrylonitrile) fibers containing silver nanoparticles. *Materials Letters*. 59(23):2977-2980.

Moreno-Villoslada I. and B.L. Rivas. 2002. Metal ion enrichment of a water-soluble chelating polymer studied by ultrafiltration. *Journal of Membrane Science*. 208(1-2): 69-73.

Nasef, M.M. 2004. Application of Electron Beam for Preparation of Membranes. *Nippon Genshiryoku Kenkyujo JAERI, Conf Journal*. 37-54.

Ofsthun, N. J., P.J. Soltys, G.A. Kunas. 1999. Affinity membrane system and method of using same. U.S. Patent No. 5,871,649.

Ramakrishna, S. W.-E. Teo, T.-C. Lim (Eds). 2005. Introduction to Electrospinning and Nanofibers. World Scientific Publishing Company, Singapore.

- Ramakrishna, S., K. Fujihara, W.-E. Teo, T. Yong, Z. Ma, R. Ramaseshan. 2006. Electrospun nanofibers: solving global issues. *Materials Today*. 9(3): 40-50.
- Rautenbach R. and A. Groeschl. 1990. Separation Potential of Nanofiltration Membranes. *Desalination*. 77(1-3): 73-84.
- Rivas, B.L., E.D. Pereira, I. Moreno-Villoslada. 2003. Water-soluble polymer–metal ion interactions. *Progress in Polymer Science*. 28(2): 173-208.
- Rivas, B.L., S.A. Pooley, E.D. Pereira, A. Maureira. 2006. Water-Soluble Polyelectrolytes with Metal Ion Removal Ability by Using the Liquid Phase Based Retention Technique. *World Polymer Congress - MACRO 2006*. 245-246(1): 116-122.
- Sang, Y., F. Li, Q. Gu, C. Liang, J. Chen. 2008. Heavy metal contaminated groundwater treatment by a novel nanofiber membrane. *Desalination*. 223:349-360.
- Smith B.F. 1993. *Actinide separations for advanced processing of nuclear waste: Annual Report 1993*. Report LA-UR-93-4017, Los Alamos National Laboratory.
- Smith, B.F., T.W. Robinson, J.W. Gohdes. 1995. Water-Soluble Polymers and Composition Thereof. U.S. Patent DOE No. S-78, 350.
- Tomida T., T. Inoue, K. Tsuchiya, S. Masuda. 1994. Concentration and/or removal of metal ions using a water-soluble chelating polymer and a microporous hollow fiber membrane. *Industrial and Engineering Chemistry Research*. 33:904-906.
- Van der Bruggen B. and C. Vandecasteele. 2003. Removal of pollutants from surface water and groundwater by nanofiltration: overview of possible applications in the drinking water industry. *Environmental Pollution*. 122(3): 435-445.
- Zou, H., Q. Lou, D. Zhou. 2001. Affinity membrane chromatography for the analysis and purification of proteins. *Journal of Biochemical and Biophysical Methods*. 49(1-3):199-240.